

# Ocean Color Reveals Phase Shift Between Marine Plants and Yellow Substance

Chuanmin Hu, Zhongping Lee, Frank E. Muller-Karger, Kendall L. Carder, and John J. Walsh

**Abstract**—Daily high-resolution Sea-viewing Wide Field-of-view Sensor (SeaWiFS) images of the central North Atlantic Ocean (1998–2003) show that temporal changes in the absorption coefficient of colored dissolved organic matter (CDOM) or “yellow substance” follow changes in phytoplankton pigment absorption coefficient in time. CDOM peaks (between January and March) and troughs (late summer and fall) followed pigment peaks and troughs by approximately two and four weeks, respectively. This phase shift is additional strong evidence that CDOM in the marine environment is derived from phytoplankton degradation. The common assumption of linear covariation between chlorophyll and CDOM is a simplification even in this ocean gyre. Due to the temporal changes in CDOM, chlorophyll concentration estimated based on traditional remote sensing band-ratio algorithms may be overestimated by about 10% during the spring bloom and underestimated by a similar 10% during the fall. These observations are only possible through use of synoptic, precise, accurate, and frequent measurements afforded by space-based sensors because *in situ* technologies cannot provide the required sensitivity or synoptic coverage to observe these natural phenomena.

**Index Terms**—Biogeochemical cycle, colored dissolved organic matter (CDOM), ocean color, phase shift, phytoplankton, remote sensing, sea surface reflectance.

## I. INTRODUCTION

**C**OLORED dissolved organic matter (CDOM), also commonly called yellow substance or Gelbstoff, is the colored fraction of the dissolved organic matter (DOM) pool in the sea [11]. The importance of CDOM in carbon cycling and light regulation in the marine environment is well recognized (see review by [12] and references therein). CDOM strongly absorbs ultraviolet (UV) and blue light, and therefore affects phytoplankton photosynthesis and the ecosystem [22]. CDOM may be degraded or bleached by sunlight [23], a transformation that releases carbon in the form of  $\text{CO}_2$  and CO.

Despite recent progress in understanding the biogeochemistry of CDOM in marine waters, the origin of CDOM in the open ocean has largely remained a mystery. Some argue that CDOM in the sea is mainly of terrestrial origin [7], while others consider terrigenous DOM to be only a small fraction of total marine DOM [19], [27]. A consideration of loss processes leads to the conclusion that <50% of the estuarine supply of CDOM remains on continental shelves [10]. Some suggest that marine

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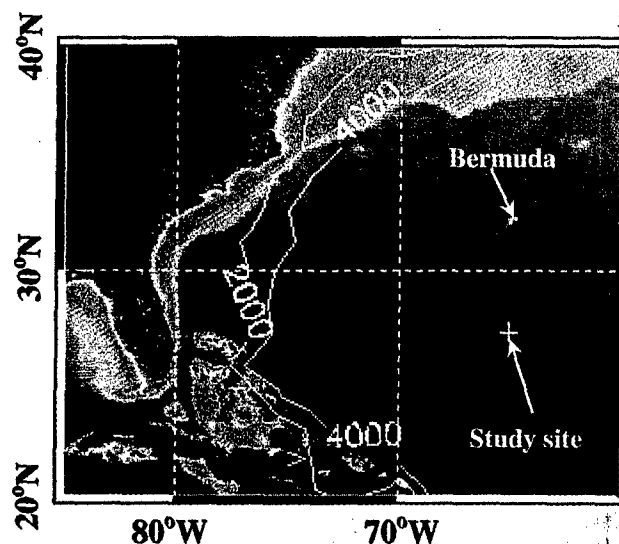


Fig. 1. Western North Atlantic portion of the subtropical gyre, with the study location marked by a cross (27.5°N 65°W). Image is a SeaWiFS chlorophyll concentration map overlaid with the 2000- and 4000-m bathymetry lines.

CDOM is a by-product of *in situ* algal cell degradation (e.g., [4]), zooplankton grazing [21], or microbial activity [25], [26]. These conclusions are largely based on laboratory experiments or limited field samples, from which it is difficult to extrapolate to ocean basin scales.

Satellite-borne sensors that measure the visible sea spectral reflectance (VSSR) (or ocean color) are particularly suited for synoptic (millions of square kilometers per satellite pass) and frequent (near daily) observations of important bio-optical properties of the surface ocean. Recent algorithms seek to partition the VSSR signal into various components, for example to accurately derive absorption coefficients of phytoplankton pigments ( $a_{ph}$ ) and CDOM/detritus ( $a_{CDM}$ ) (e.g., [13], [16], and [29]). It is difficult to partition  $a_{CDM}$  explicitly into absorption coefficients of CDOM ( $a_g$ ) and detritus ( $a_d$ ) due to the similarity of their spectral shapes. However, because  $a_d$  usually contributes 5% to 20% or less to  $a_{CDM}$  in the deep open ocean [25],  $a_g$  may be represented by  $a_{CDM}$  in studies of offshore processes. To date, however, the relationship between satellite-derived  $a_{ph}$  and  $a_g$  has not been well documented even for the open ocean.

A hypothesis of general oceanographic interest is whether the bulk of the CDOM found in the marine environment is a by-product of algal biological degradation or not. A close relationship between temporal changes in  $a_g$  and  $a_{ph}$  would help understand the relationship between CDOM and phytoplankton. However, in the past it has been impossible to explore this relationship in the open ocean due to limitations of *in situ* sampling frequency, the low sensitivity of ship-based observations, and the simple algorithms used to study changes in ocean color. New

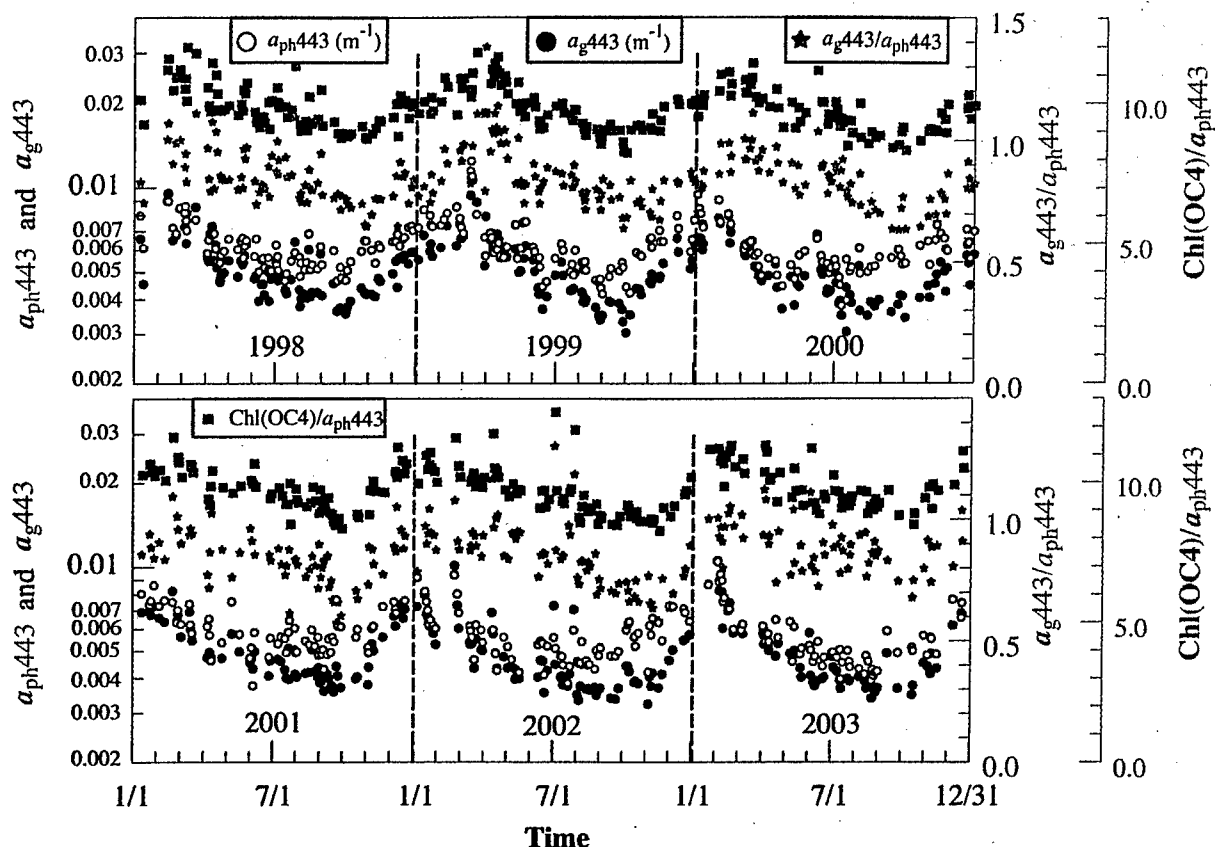


Fig. 2. Absorption coefficients of phytoplankton pigment ( $a_{ph443}$ ,  $m^{-1}$ ) and CDOM ( $a_{g443}$ ,  $m^{-1}$ ) for the oligotrophic surface ocean at  $27.5^{\circ}N$   $65^{\circ}W$  (Fig. 1), derived from high-resolution (1-km) daily SeaWiFS data between 1998 and 2003 with a quasi-analytical algorithm [16]. Also shown are the  $a_{g443}/a_{ph443}$  ratio, as well as the ratio between chlorophyll concentration estimated from the band-ratio OC4v4 algorithm [ $Chl(OC4)$ ] and  $a_{ph443}$ .

high-quality satellite observations of the VSSR and increasingly sophisticated algorithms allow us to revisit this basic hypothesis.

## II. DATA AND METHODS

To minimize the impact of lateral exchanges and terrigenous inputs of colored organic and other materials on our conclusions, our study was conducted in the southern Sargasso Sea, at  $27.5^{\circ}N$   $65^{\circ}W$ . This is in the western portion of the North Atlantic subtropical gyre, where waters exhibit homogeneous optical properties over horizontal distances exceeding hundreds of kilometers (Fig. 1). This region features some of the clearest water in the world.

Data from the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) collected during 1998–2003 were processed with the SeaDAS4.6 software released by NASA's Goddard Space Flight Center. The derived remote sensing spectral reflectance data ( $R_{rs}(\lambda)$ ,  $sr^{-1}$ ), after a rigorous quality control process (e.g., pixels with suspicious flags were removed, and a  $15 \times 15$  box centered at the location was used to remove sensor/algorithm noise [14]), were then used as input to a quasi-analytical algorithm [16] to estimate  $a_{ph443}$  and  $a_{g443}$  (where 443 is the band center wavelength in nanometers). Briefly, total absorption and backscattering coefficients at 555 nm were first estimated empirically and analytically. The coefficients at other wavelengths were then derived using an empirical estimate of particle backscattering spectral shape.  $a_{ph443}$  and  $a_{g443}$  were analytically derived from the total absorption coefficients at 412 and 443 nm. In this last step, a specific CDOM absorption spectral

slope,  $S$ , was assumed to be constant and equal to  $0.02nm^{-1}$ . A sensitivity analysis was conducted to test this assumption, and the results are discussed below. Chlorophyll-*a* concentration ( $Chl$ ) was derived using the OC4v4 algorithm [28].

## III. RESULTS AND DISCUSSION

Fig. 2 shows the SeaWiFS time series of  $a_{g443}$ ,  $a_{ph443}$ ,  $a_{g443}/a_{ph443}$ , and the  $Chl/a_{ph443}$  ratio for our Sargasso Sea location. A seasonal cycle is evident in all parameters, with winter maxima and late summer minima. There is little interannual variation, suggesting that the oligotrophic ocean gyre may be used to monitor long-term stability of future satellite sensors.

The high temporal resolution and the length of the series reveal a lag in  $a_{g443}$  relative to  $a_{ph443}$ . The lag is more manifest when all data of 1998–2003 are averaged to produce a weekly climatology [Fig. 3(a)]. Correlation analysis based on the weekly climatology shows that  $a_{g443}$  maxima lagged  $a_{ph443}$  maxima by about two weeks during winter-spring (week 49–19). The minimum  $a_{g443}$  lags  $a_{ph443}$  by about 4–5 weeks during summer-fall (week 26–48) (Fig. 4). The lag, or phase shift, between  $a_{g443}$  and  $a_{ph443}$  is more manifest when summer-fall (week 26–48) lows and winter-spring (week 49–19) highs are treated separately, because of the various processes that drive these temporal changes (see below). The horizontal lines in Fig. 4 correspond to the 95% significance levels calculated using a “phase randomization” method [8]. Correlation coefficients above these lines indicate that the two time-series are significantly correlated. The same analysis

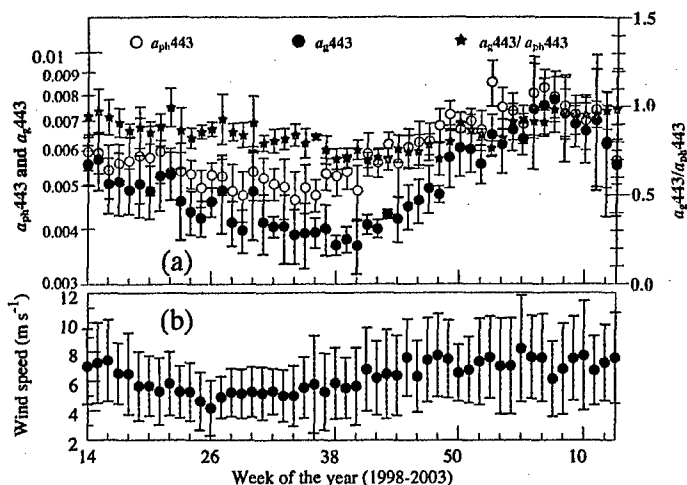


Fig. 3. (a) Weekly climatology (1998–2003) of  $a_{ph443}$  (per meter) and  $a_{g443}$  (per meter) for the oligotrophic surface ocean at  $27.5^{\circ}N$   $65^{\circ}W$  (Fig. 1). (b) Average wind speed for the corresponding weeks, obtained from the National Center for Environmental Prediction. Error bars indicate standard deviation. In order to show the peaks and troughs more clearly, the week starts from 14 to 52, and then continues to week 1.

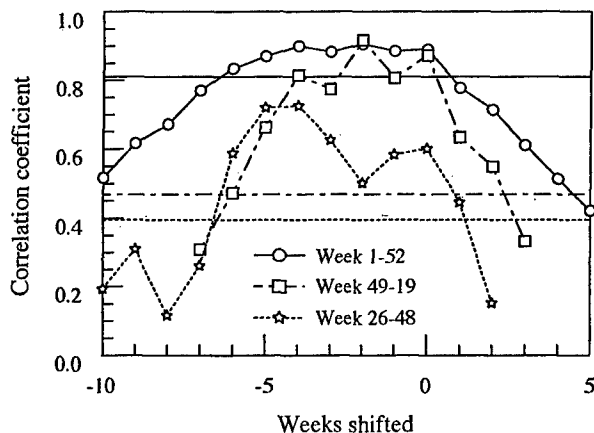


Fig. 4. Correlation coefficients between  $a_{ph443}$  (per meter) and  $a_{g443}$  (per meter) from the weekly climatology data [Fig. 3(a)]. Three analyses were performed for the entire dataset (week 1–52), winter-spring (week 49–19), and summer-fall (week 26–48), respectively. Negative number means that  $a_{g443}$  is behind  $a_{ph443}$ . The horizontal lines are the corresponding 95% significance level for the correlation (see text for more details).

could not be applied to the original daily data because they were unequally spaced in time, and interpolation in temporal space would create additional uncertainties due to residual noise in the daily data. Although the correlation coefficient from the weekly climatology would be different than from the daily data, our focus is on the relative changes versus time. Therefore the results should be valid.

The phase shift suggests that the surface CDOM peak is likely the result of phytoplankton growth and degradation. This may help explain the findings of Nelson *et al.* [25] and Siegel and Michaels [30] where less-frequent *in situ* data from the U.S. Joint Global Ocean Flux Study's Bermuda Atlantic Time-Series Study (BATS) suggested that nonliving materials (dissolved and particulate) did not appear to covary with phytoplankton over the course of about two years in the upper 60 m. Clearly, the lag would reduce the linear correlation between these variables measured at the same time. Also, the satellite integrates the signal over the first optical depth in estimating the absorption

coefficient, or about the upper 40–50 m of the water column at this clear water site, while a laboratory instrument is typically restricted to 10-cm pathlength sample cells to measure  $a_g$ . Therefore, the satellite sensor is more sensitive than a laboratory instrument, allowing for better resolution of synoptic changes.

The phase shift between  $a_{g443}$  and  $a_{ph443}$  was manifested in the seasonality of the  $a_{g443}/a_{ph443}$  ratio, which suggests that after a bloom CDOM is destroyed at a lower rate than phytoplankton degradation. Similarly, while the increase and decrease in  $a_{ph}$  are relatively symmetrical around a bloom,  $a_g$  buildup and decay are not. CDOM increases rapidly and peaks approximately in February–March immediately after the bloom, but then decays more slowly through September and October.

Can the similar  $a_{ph}$  and  $a_g$  patterns be simply a matter of coincidence with no dependence between each other? Deeper wind-driven and convective mixing [Fig. 3(b)] in the region during winter brings deep nutrients to the surface, and the availability of light stimulates higher phytoplankton growth following the classical Sverdrup [32] model. We may speculate that mixing may, at the same time, introduce deep unbleached CDOM to surface waters. However, if this is a dominant process, we would expect simultaneous increases in both  $a_{ph}$  and  $a_g$  or even a slight lead in  $a_g$  in the winter, since it may take time for phytoplankton to develop the bloom. Our observations (Figs. 2 and 3) do not support this hypothesis. Further, correlation between climatological winds and  $a_g$  (0.63,  $n = 52$ ) is lower than between wind and  $a_{ph}$  (0.72,  $n = 52$ ), again suggesting that mixing does not force the phase shift.

Are the lag patterns due to an artifact introduced because of the constant spectral slope  $S = 0.02 \text{ nm}^{-1}$  used in the quasi-analytical algorithm? In nature,  $S$  ranges from approximately  $0.012 \text{ nm}^{-1}$  in coastal waters to  $0.034 \text{ nm}^{-1}$  in the open ocean (e.g., [1], [9], and [25]). Because detrital particles tend to have similar spectral absorption shapes but lower spectral slope values, we used an average of  $S = 0.02 \text{ nm}^{-1}$  in our study, which is consistent with the observations made in the Sargasso Sea [25]. For  $a_g < 0.01 \text{ m}^{-1}$  (below instrument detection limits for 443 nm)  $S$  can only be inferred from the UV wavelengths, and it is unclear how it changes when CDOM is photodegraded (bleached). Moran *et al.* [24] reported that for coastal waters,  $S_{UV}$  increased by 6% to 10% when CDOM was 60% bleached. We therefore performed a sensitivity analysis by changing  $S$  between  $0.018$  and  $0.022 \text{ nm}^{-1}$  either randomly or systematically (i.e., increase  $S$  from  $0.018$  in the spring to  $0.022$  in the fall). Results show that the magnitudes of  $a_{ph}$  and  $a_g$  were sensitive to the choice of  $S$ , but the temporal patterns and lags between these properties remained independent of these changes in  $S$ .

Carder *et al.* [3] had documented an episode of  $a_g$  increase after the rapid development and peaking of chlorophyll and  $a_{ph}$  in a coastal phytoplankton bloom on the west Florida Shelf, with a lag time of approximately 1.5 weeks. Our results show that similar lags exist in the oligotrophic ocean. Loisel *et al.* [17] showed temporal lag patterns in the particulate backscattering coefficient versus chlorophyll concentration (band-ratio algorithm) from SeaWiFS in the North Atlantic, consistent with our findings here. Siegel *et al.* [31] reported global CDM patterns as well as CDM time-series from BATS. Our time-series data show

lower values but similar winter-spring maxima and summer-fall minima as BATS. Our location (~500 km south of Bermuda) is closer to the gyre center and is characterized by clearer, less productive water. Here, the uncertainties in the magnitude of  $a_{ph}$  and  $a_g$  estimates are likely to be smaller, which helps our study of the relationship between phytoplankton blooming and CDOM generation.

Since neither vertical mixing nor horizontal advection, nor artifacts in bio-optical algorithms, cause the lag observed between the phytoplankton and CDOM, we present the following hypothesis to explain the temporal patterns observed. First, CDOM is produced as a result of phytoplankton grazing and cell degradation, causing a lag in the  $a_g$  maxima. Then, CDOM is slowly destroyed through photodegradation near the surface [23]. As summer starts, phytoplankton concentration decreases due to nutrient limitation but continues to generate CDOM, which in turn undergoes bleaching and photodegradation as UV light intensity increases in a seasonal intensification. The complex interaction between these processes leads to an apparently slower rate of decrease in CDOM during the summer than the rate of increase after the winter-spring phytoplankton bloom.

Our results (Figs. 2–4) have several significant implications. First, they provide indirect evidence that a significant portion of CDOM in the surface layer of the open ocean originates from phytoplankton. Phytoplankton excretion, bacterial processing of decomposing organic matter, and sloppy feeding by zooplankton are all possible sources of CDOM. During the more sparsely sampled *in situ* time series at BATS, the depth maxima of the dissolved organic carbon (DOC) and the spring bloom of diatomaceous phytoplankton coincided [20], such that cell lysis, uncoupled from the heterotrophic sources of zooplankton grazing and bacterial remineralization, was inferred as the major source of DOC. In the northern Sargasso Sea, macrozooplankton dominate during spring, and limited sampling suggests that herbivore biomass has a month time lag following phytoplankton [18]. Sampling at a faster rate from daily satellite observations, our phase shift of weeks, rather than months, instead suggests that marine CDOM may mainly be derived from lysis of phytoplankton cells, with a fraction derived from zooplankton grazing and excretion.

The second implication is the impact of the phase shift on the bio-optical band-ratio algorithm used to estimate chlorophyll concentration from remote sensing observations (for oligotrophic waters the ratio is typically between  $R_{rs}$  at 443 and 555 nm, as for example with the OC4v4 algorithm of [28]). Clearly, any bias in the chlorophyll estimates is of fundamental relevance to estimating primary production (see [2] and references therein). The ratios of  $a_{g443}/a_{ph443}$  and  $Chl(OC4)/a_{ph443}$  clearly show seasonal variability (Fig. 2). This implies that if chlorophyll is linearly proportional to  $a_{ph443}$ , then the band-ratio OC4 algorithm will overestimate the magnitude and possibly the duration of the spring bloom in the Sargasso Sea. We estimate that this overestimate of chlorophyll is upward of 10% during the spring. Similarly, there is an underestimate of chlorophyll during the fall of up to 10%.

The bio-optical artifact introduced by this seasonality may require reexamining previous inferences about biogeochemical and physical processes in the subtropical gyres. For example, color anomalies in the subtropical gyres have been hypothesized to be related to planetary (Rossby) waves. Some argue that

the color anomaly may be due to local phytoplankton growth stimulated by wave-pumped deep-water nutrients [33], but others argue that the cause is detrital particles advected horizontally [5], [15]. The ability to separate CDOM from chlorophyll, the lag observed between the two, and the new knowledge that the lag confounds the timing and magnitude of the variability in the historical OC4-derived chlorophyll concentration suggests that these previous hypotheses require further research.

Finally, from the viewpoint of biogeochemical modeling (e.g., [34]), the phase shift of  $a_g$  relative to  $a_{ph}$  for the deep sea has important implications. Deuser *et al.* [6] found that seasonal variability in surface chlorophyll concentration, as derived using band ratios from Coastal Zone Color Scanner data, was reflected in the sediment flux, and that flux at depth lagged surface production by about one and a half months. If, however, prior satellite estimates of chlorophyll were not a measure of the actual chlorophyll concentration, but reflect a convolution of lagged pigment and CDOM stocks, the conclusions of Deuser *et al.* [6] may also need to be revised. The true time difference between particle export and surface chlorophyll may be as long as two, or two and one-half months, relative to previous estimates. Particle settling rates in the subtropical ocean may be much slower, or of order 70 m per day, instead of the 100 m per day, estimated from those seminal studies.

#### IV. CONCLUSION

With daily high-resolution SeaWiFS data and a recently developed algorithm, we document a lag (phase shift) between the temporal patterns of phytoplankton pigments and CDOM in the North Atlantic subtropical gyre. Lag times are about two weeks and 4–5 weeks for the winter-spring maxima and summer-fall minima, respectively, in these variables. The phase shift suggests that CDOM is related to phytoplankton growth, grazing, and degradation, and our concept of linear covariation between the two (the basis for the band-ratio chlorophyll algorithms) may need to be revisited. The discovery of the phase shift demonstrates the significance of satellite observations in process-related studies. Advancing and using this technology will continue to move our understanding of global biogeochemical cycles forward.

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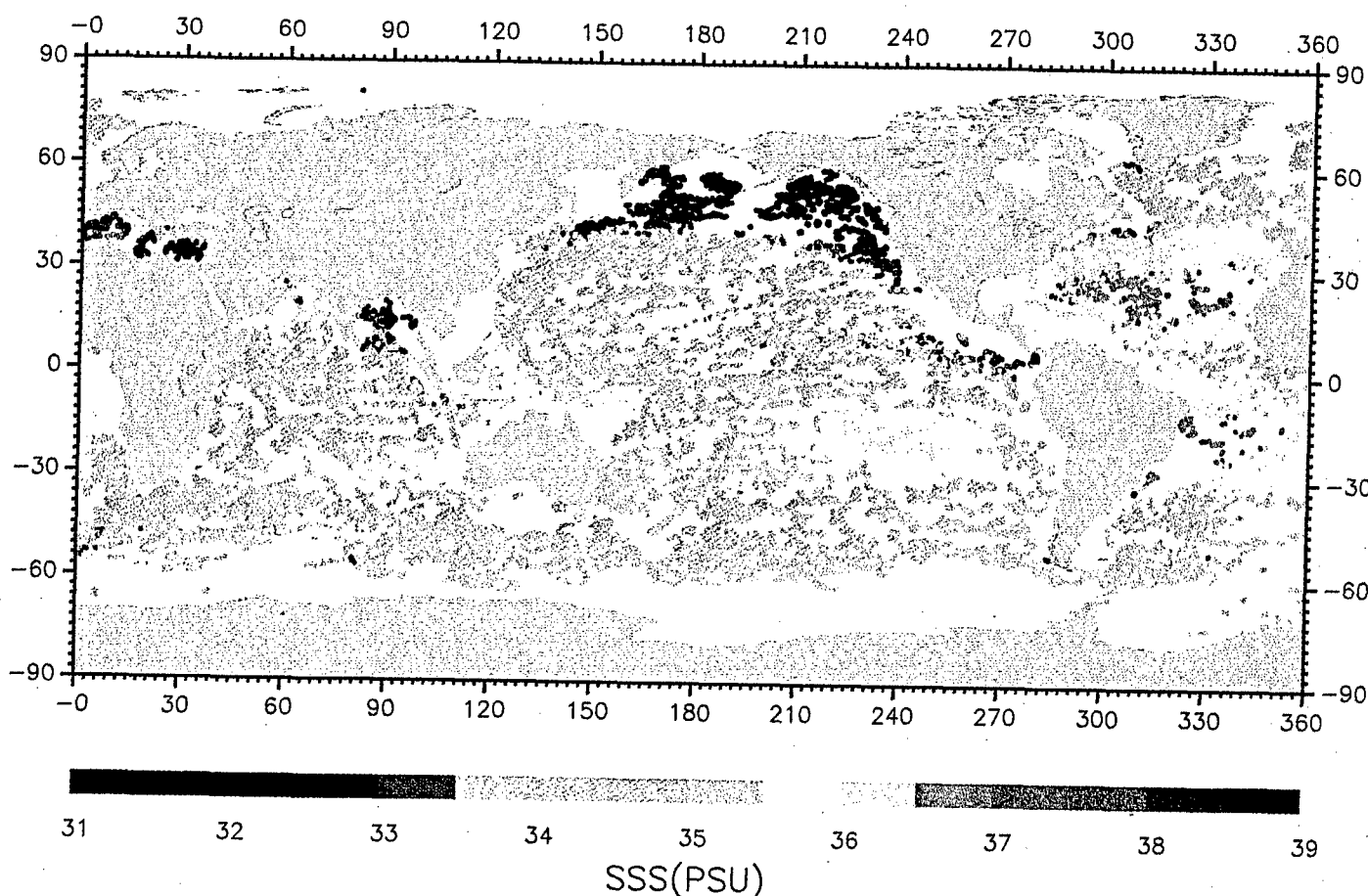
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14. ABSTRACT Daily high-resolution Sea-viewing Wide Field-of-view Sensor (Sea WiFS) images of the central North Atlantic Ocean (1998-2003) show that temporal changes in the absorption coefficient of colored dissolved organic matter (CDOM) or "yellow substance" follow changes in phytoplankton pigment absorption coefficient in time. CDOM peaks (between January and March) and troughs (late summer and fall) followed pigment peaks and troughs by approximately two and four weeks, respectively. This phase shift is additional strong evidence that CDOM in the marine environment is derived from phytoplankton degradation. The common assumption of linear covariation between chlorophyll and CDOM is a simplification even in this ocean gyre. Due to the temporal changes in CDOM, chlorophyll concentration estimate based on traditional remote sensing band-ratio algorithms may be overestimated by about 10% during the spring bloom and underestimated by a similar 10% during the fall. These observations are only possible through use of synoptic, precise, accurate, and frequent measurements afforded by space-based sensors because <i>in situ</i> technologies cannot provide the required sensitivity or synoptic coverage to observe these natural phenomena.						
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